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Studies on the electrochemical and electrocatalytic behavior of phthalocyanines

Theses of doctoral dissertation

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Introduction

Investigations of the electrochemical behavior of phthalocyanines (Pc) have been in the foreground of research during the last decades especially as a catalyst of the oxygen reduction reaction (ORR). In my doctoral work measurements were carried out, which are important to prepare better catalysts. Main focus point of these studies was to understand the redox behavior of the Pcs using Electrochemical Quartz Crystal Nanobalance (EQCN). This work is very important and useful, because most articles about Pcs deal with ORR catalytic activity of the Pc layers and with preparation new Pcs or composites of Pcs with carbon materials and conducting polymers. My work supplements these studies with information about the redox reactions of the layers. The EQCN is one of the most proper technique for that goal, because we can get in-situ information about nano-scale changes in the layer.

An electrochemical quartz crystal nanobalance has been used to study the redox behavior of iron phthalocyanine (FePc), palladium phthalocyanine (PdPc), phthalocyanine (hydrogen phthalocyanine, HPc), cobalt phthalocyanine (CoPc) and copper phthalocyanine-3,4′,4″,4‴-tetrasulfonic acid (CuPcTs) in aqueous solutions at different pH values. The shape of the cyclic voltammograms, i.e., the number of oxidation and reduction peaks, their relative ratios, effect of several factors such as the potential limits, presence and absence of oxygen, the nature and the concentration of the electrolyte were analyzed.

The conductive behavior of Pcs was analyzed by measuring the 2-point and 4-point resistances of the Pc layers simultaneously. The importance of these measurements is that Pcs are organometallic compounds, and their conductivity is much lower than metal catalyst (such as platinum).

This can be one of the limits their feasibility. Resistances of several Pcs (FePc, PdPc, polyCuPc and HPc) were measured in this work at different pHs as a function of potentials.

The catalytic activity of the Pcs toward ORR was analyzed with rotating disc electrode (RDE) in acidic and alkaline medium as well. FePc, PdPc, polyCuPc, CoPc and HPc were analyzed.

Results and conclusions

Nanogravimetric measurements

Electrochemical and nanogravimetric studies of iron phthalocyanine microparticles

1. In the case of oxidation of central metal ion formation and oxidation of dimeric species were assumed. The process is accompanied with protonation / deprotonation and counter ion flow both, because the peak potentials shift with pH changes. The nanogravimetric changes were proportional to the molar mass of the ions. At more positive potentials the other iron ion of the dimer oxidizes as well. This peak did not show any pH dependence.
2. Redox reactions of the Pc ring are more pH sensitive indicating the importance of the protonation in these processes. Pc^{2-} / Pc^{3-} transformations are reversible processes taking place without substantial structural changes. Pc^{2-} / Pc^{-} transformation can also be realized, however, due to the structural changes, it leads eventually to the delamination / dissolution of the FePc layer. Pc^{3-} / Pc^{4-} is a reversible redox process; however, it is accompanied with a phase transition. The mass changes during the redox transformations can be elucidated by considering the sorption-desorption of counterions and water molecules in / from the FePc layer. The pH dependence of the peak potentials of all processes that are related to the redox reactions of Pc ring revealed that protonation and deprotonation reactions also

occur. Phase transition appears in the separation of the peak potentials and in the large hysteresis of the frequency curves.

3. It has been proven that adducts with O_2 are formed. The reduction of oxygen and Fe^{3+} ions start when Fe^{3+} ions of FePc had been converted to Fe^{2+} during reduction.

Electrochemical and nanogravimetric studies of palladium phthalocyanine microcrystals

4. In aqueous acidic media PdPc is protonated in its reduced form and counterions compensate the positive charges, therefore those are already present in the surface layer. During oxidation H_3O^+ ions leave the layer, and the exchange of anions is a minor process in acid media except at high positive potentials. With increasing pH the incorporation and expulsion of counterions during the oxidation and reduction processes, respectively, will become the dominant process.
5. Phase transitions also occur during the electrochemical transformations which manifest itself in the large separation of respective pair of waves. The phase transition also influences the EQCN response because the surface structural changes causing strain in the surface layer, and it leads to anomalously large frequency changes.
6. Scan-rate dependence analysis shows that solvent sorption / desorption accompanies the charging / discharging processes and the phase transitions. At fast polarization the incorporation process is incomplete, because the solvation shell of the ions is dropped behind.

Electrochemical and nanogravimetric studies of phthalocyanine microcrystals

7. In case of HPc it was found that similar to PdPc the oxidation of the layer happens in two steps. First a protonation / deprotonation takes place, and the incorporation of the counter ions starts at higher potentials. At the reduction of the HPc beside cations protons have also a major role. Phase transition takes place as well.
8. In alkaline medium we have to take into account, that at high pH values the central hydrogen atoms of the HPc can be replaced by the cations spontaneously. The conformation changes during this reaction can explain the anomalous frequency changes in alkaline medium.

Conductivity studies on phthalocyanine layers

9. It was found, that the resistance of metal phthalocyanines is two orders of magnitude lower than that measured for HPc's in air. R_2/R_4 ratio was close to ideal 3.0 in case of FePc and polyCuPc which indicates that the geometric and adhesive properties of the layer are satisfying.
10. It was shown that Pcs, in which the center ion does not participate in the redox transformations, have three conductive states. In neutral state the resistance is very high, and when oxidation / reduction takes place the conductivity increases heavily. When counter ions enter the layer during the electrochemical reactions the resistance also decreases. The changes of the resistance are in good correlation with changes on the voltammogram and frequency curves. The pH

dependence of the resistance meets the expectations from Nernst equation and conductivity of the electrolytes.

11. In case of FePc five conductive states were found. In addition to the already described ones a local minimum at Fe^{2+} / Fe^{3+} and a local maximum at the formation of the dimer were measured. In alkaline medium very large resistance was measured, which can be explained by reaction between central iron ions and OH^- ions leading to formation of non-conductive species.
12. Conductive properties of polyCuPc was better than those for other Pcs because of the extended delocalized electron system. The changes of polyCuPc's resistance are similar to the behavior of conductive polymers. In this case the changes of the conductance are proportional to the potential. At every pH the increase of the resistance starts after the oxidizing of the Pc ring.

Catalytic activity of phthalocyanines on Oxygen Reduction Reaction

13. It was found, that Pcs are much more effective catalysts of oxygen reduction reaction in alkaline media. In acidic solutions limiting current could not be measured. FePc and PdPc catalyze the 4-electron process, while CoPc, polyCuPc and HPc catalyze the 2-electron process.
14. Both in acidic and alkaline media FePc and PdPc were the best catalysts, despite the fact that in sulfuric acid almost 200 mV higher overvoltage compared to platinum was measured. In alkaline medium they were almost as good catalyst as platinum.

Publications

The Dissertation is based on the following articles:

1. G. Inzelt, Á. Nemes, Á. Sajti: Study of the surface mass changes during the redox transformations of copper(II) phthalocyanine-tetrasulfonic acid on gold in acidic media. *J. Solid State Electrochem.* (**2017**) doi:10.1007/s10008-017-3547-x
2. Á. Nemes, Gy. Inzelt: Electrochemical and nanogravimetric studies of iron phthalocyanine microparticles immobilized on gold in acidic and neutral media. *J. Solid State Electrochem.* 18 (**2014**) 3327-3337.
3. Á. Nemes, C.E. Moore, Gy. Inzelt: Electrochemical and nanogravimetric studies of palladium phthalocyanine microcrystals. *J. Serb. Chem. Soc.* 78 (**2013**) 2017-2037

Other scientific papers:

1. B. B. Berkes, Á. Nemes, C.E. Moore, F. Szabó, Gy. Inzelt: Electrochemical nanogravimetric study of the electropolymerization of 6-aminoindole and the redox transformations of the polymer formed in aqueous media. *J. Solid State Electrochem.* 17 (**2013**) 3067-3074
2. Á. Kriston, B. B. Berkes, P. L. Simon, Gy. Inzelt, K. Dobos, Á. Nemes: Unusual surface mass changes in the course of the oxygen reduction reaction on platinum and their explanation by using a kinetic model. *J. Solid State Electrochem.* 16 (**2012**) 1723-1732
3. M. Balaskó, L. Horváth, Á. Horváth, Á. Kriston, Á. Nemes: Tüzelőanyag cellák működés közbeni vizsgálata dinamikus

neutron radiográfia alkalmazásával [Study of fuel cell in service applying the dynamic neutron radiography]. *Anyagvizsgálók Lapja* 21 (**2011**) 34-38

Presentations, Conference Participations

1. Á. Nemes, Á. Kriston, Gy. Inzelt: Analysis of the effects of the Nafion content for the microstructure of a PEMFC by using a two dimensional model. *HYCELTEC 2013*, Lisboa, Portugal, **2013**
2. Á. Nemes, Á. Kriston, G. Inzelt: Analysis of the porosity, agglomerates' size and exchange current density of a PEMFC by using a two-dimensional model. *63rd Annual Meeting of the International Society of Electrochemistry*, Prague, Czech Republic, **2012**
3. M. Balaskó, L. Horváth, A. Horváth, Á. Kriston, Á. Nemes: Tüzelőanyag cellák működés közbeni vizsgálata dinamikus neutron radiográfia alkalmazásával. *Roncsolásmentes Anyagvizsgálok konferenciája*, Eger, Hungary, **2011**
4. Á Nemes, Á Kriston, G Inzelt, T Szabó: Analysis of the effects of variation of the MEA microstructure at different Pt/Nafion ratios, pressures and temperatures.. *61st Annual Meeting of the International Society of Electrochemistry*, Nice, France, **2010**

Informative articles

1. Kriston Á., Szabó T., Berkes B. B., Nemes Á.: Városi Közlekedés Hidrogénalapon. *Környezetvédelem* 17 (**2009**) 16-17.

2. Nemes Á.: Pozitív AIDS teszt-ok a pánikra? Avagy ki tört be a házamba. *Természet Világa* (**2008**) 139. évf. 3. sz. XXXIII-XXXV.
3. Nemes Á.: A Pannonhalmi Ásványtár története. *Természet Világa* (**2007**) 138. évf. 1. sz. V-VI.
4. Nemes Á.: A négyszín-sejtésről. *Természet Világa* (**2006**) 137. évf. 10. sz. CXLVII-CXLIX.